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(54) Title: METHOD OF SYNTHESIS OF CARBON NANOMATERIALS

(57) Abstract: A method of synthesis of carbon nanomaterial comprises the steps of: preparing a solution of a catalyst or a catalyst precursor in a supercritical fluid, or of a supercritical fluid in a catalyst or a catalyst precursor, the catalyst or catalyst precursor being capable respectively of catalysing the formation of carbon nanomaterials from a carbon source or of reacting to form a catalyst having such a capability; expanding the solution to produce particles of catalyst or catalyst precursor; and heating the catalyst or catalyst precursor particles with a carbon source to produce carbon nanomaterials.

METHOD OF SYNTHESIS OF CARBON NANOMATERIALS

The present invention relates to a method of synthesis of carbon nanomaterials such as fullerenic nanostructures, for example single or multi-walled carbon nanotubes, in particular to a method of synthesis of carbon nanomaterials by chemical vapour deposition (CVD).

The remarkable mechanical and electronic properties exhibited by carbon nanotubes have encouraged efforts to develop mass production techniques. As a result, carbon nanotubes are becoming increasingly available, and more attention from both academia and industry is focused on the application of carbon nanotubes in bulk quantities. These opportunities include the use of carbon nanotubes as a conductive filler in insulating polymer matrices, and as reinforcement in structural materials. Other potential applications exploit the size of carbon nanotubes as a template to grow nano-sized, and hence ultra-high surface-to-volume ratio, catalysts or aim to combine carbon nanotubes to form nano-electronic elements.

The high cost and low production volume of carbon nanotubes are at present prohibitive for them to be used as a filler material in most large-scale structural and electrical applications.

Such materials have been produced previously using various approaches including the laser or arc-discharge ablation of a carbon/catalyst mixture target.

For larger scale synthesis, the most promising methods have been based on chemical vapour deposition (CVD). CVD typically uses a cheap feedstock and has relatively low energy requirements, and has therefore attracted interest for the purposes of bulk synthesis. In CVD methods, a carbon containing gas is decomposed at high temperatures under the influence of a finely divided catalyst (usually iron, nickel, cobalt or other transition metals or alloys).

Catalyst particles may be manufactured in situ by the decomposition of metalloorganic compounds or may be inserted into the CVD furnace on a fixed substrate (W. E. Alvarez et al., Carbon 39 (2001) 547-558; WO00/17102; WO00/73205). For

the growth of small nanotubes and single-walled nanotubes in particular, very small metal clusters (around 1 nm) are required.

For the purposes of bulk synthesis, continuous injection  
5 of a catalyst precursor is preferred. This type of injection is currently carried out by dissolving the precursor in a hydrocarbon solvent (for example ferrocene in xylene) and pumping the solution into the furnace (L. Ci et al., Carbon 39 (2001) 329-325), or by subliming the solid precursor directly  
10 (WO00/26138).

The use of a hydrocarbon solvent introduces an additional active material into the system. The hydrocarbon solvent may be used as the carbon source for the CVD reaction. However, hydrocarbons which are good solvents for the  
15 precursor are not in general the same hydrocarbons as would desirably be selected as the carbon source. Typically, the solvent will form unwanted amorphous carbon soot during thermal decomposition. The solvent will typically also have complex decomposition pathways which are difficult to control.  
20 Additionally, the enforced mixing of the hydrocarbon supply and the catalyst prevents a more optimal arrangement of the system. For example, to ensure a small catalyst particle size, it is preferable to inject cold precursor directly into hot hydrocarbon, so that there is minimal opportunity for  
25 metal cluster growth prior to nucleation of the nanotube.

Evaporation or sublimation of pure precursor material has the disadvantage that relatively large clusters of precursor tend to be produced, which produce large catalyst clusters. Furthermore, most current embodiments of pure  
30 catalyst precursor injection release a variable catalyst concentration over time.

A supercritical fluid may be strictly defined as any substance that is above its critical temperature and critical pressure. Under these conditions, the distinction between  
35 liquid and gas disappears. A supercritical fluid has stronger solvating power than a gas, but expands to fill available space. However, specialists in supercritical fluids use the term "near-critical" to describe substances which, although they have temperatures below the critical temperature and are

still liquid, display some of the useful properties of the true supercritical fluid. For the purposes of this invention, we include near-critical fluids in our definition of supercritical fluid, for example fluids at at least 50% of critical temperature, particularly at least 80% of critical temperature. The pressure should be such that the material is on the liquid side of the liquid-gas phase boundary, although it will usually be significantly higher than the critical pressure. It is preferred that the density is at least 90% of critical density.

The solvating power of supercritical fluids can often be improved by the addition of a small amount of "modifier" (eg 1 or 2 % methanol in scCO<sub>2</sub>).

For further information see J. A. Darr et al., Chemical Reviews, 1999, Vol. 99, No. 2.

US-A-6132653 describes the formation of nanopowders of yttrium stabilised zirconia (YSZ) for use in coating applications by expansion of near-critical fluid (toluene/propane) containing dissolved Zr 2-ethylhexanoate and Y 2-ethylhexanoate, and reaction of the spray thus formed. The particles so produced are of 2 to 10 nm in diameter.

The present invention provides a method of synthesis of carbon nanomaterials, comprising the steps of: preparing a solution of a catalyst or a catalyst precursor in a supercritical fluid, or of a supercritical fluid in a catalyst or a catalyst precursor, the catalyst or catalyst precursor respectively being capable of catalysing the formation of carbon nanomaterials from a carbon source or of reacting to form a catalyst having such a capability; expanding the solution to produce particles of catalyst or catalyst precursor; and heating the catalyst or catalyst precursor particles with a carbon source in a furnace to produce carbon nanomaterials.

Preferably, the carbon nanomaterial is either single-walled or multi-walled carbon nanotubes.

Because most supercritical fluid applications (such as solvation) also require that the density be close to or higher than the critical density (the mass of fluid per unit volume at the critical temperature and pressure or "critical point"

of the fluid), it is preferred that this condition is satisfied by the solution referred to above.

Preferably, the solution is expanded to produce finely dispersed catalyst precursor as it enters the furnace.

5        Preferably, the solution is expanded through an expansion nozzle. The design of the nozzle is important for optimum performance in controlling the size of catalyst particles that are formed and their interaction with the carbon source. For small size applications, an orifice size of  
10    5 to 100 micrometer, and a length of less than 1 mm, may be desirable although larger nozzles may be desirable may be appropriate for larger size applications.

For example, the nozzle is preferably arranged such that the expanding solution forms a plume parallel to the furnace  
15    walls. If the plume impinges on the wall surface it will tend to cause larger catalyst particles to form, and may expose the furnace lining to unacceptable shock.

The use of supercritical expansion (known as supercritical fluid injection molecular spray) is described,  
20    for example in US-A-4582731, US-A-4734451 and US-A-4734227.

Suitable carbon-containing compounds for use as the carbon source include carbon monoxide and hydrocarbons, including aromatic hydrocarbons, e.g. benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene or  
25    anthracene, non-aromatic hydrocarbons, e.g. methane, ethane, propane, butane, pentane, hexane, cyclohexane, ethylene, propylene or acetylene, and oxygen-containing hydrocarbons, e.g. formaldehyde, acetaldehyde, acetone, methanol or ethanol, or a mixture of two or more thereof. In preferred  
30    embodiments, the carbon-containing compound is carbon monoxide (CO), methane, ethylene or acetylene.

The carbon source may be mixed with one or more gases acting as a diluent such as inert gases, e.g. argon. It may also be mixed with non carbon containing gases which play no  
35    direct role in the nanotube forming reaction but which play a contributory role, for instance by reacting with amorphous carbon as it is formed (as a by-product) and so keeping the reaction sites on the catalyst clean and available for nanotube formation.

Gases which may be mixed with the carbon source include argon, hydrogen, nitrogen, ammonia, carbon dioxide or helium.

The gaseous effluent from the furnace may be recycled, with or without clean up.

- 5        The catalyst precursor is suitably a transition metal catalyst precursor, particularly one comprising copper (Cu),  
----- or a Group VIB transition metal (chromium (Cr), molybdenum  
         (Mo), tungsten (W)) or a Group VIIIB transition metal (iron  
         (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh),  
10        palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt))  
         or a mixture of two or more thereof. Metals from the  
         lanthanide and actinide series may also be used. Preferred  
         transition metal catalyst precursors comprise a mixture of two  
         or more of the listed metals. Particularly preferred  
15        transition metal catalyst precursors comprise Fe, Ni, Co, Mo  
         or a mixture of two or more thereof such as a 50/50 mixture  
         (by weight) of Ni and Co, or a mixture of Fe and Ni, or a  
         mixture of Fe and Mo. Any of these transition metals  
         individually or in combination with any of the other  
20        transition metals listed may be used as a catalyst for carbon  
         nanotube growth.

         The catalyst precursor is preferably a heat or light or  
plasma decomposable compound of one or more metals listed  
above.

- 25        Preferably, the catalyst precursor is an organometallic  
         compound comprising a transition metal and one or more  
         ligands. The ligands of the catalyst precursor preferably  
         ensure high solubility of the catalyst precursor in the chosen  
         supercritical fluid, preferably contain the elements C, H and  
30        O only, and preferably are simple molecules which decompose  
         without poisoning the catalyst metal or interfering with the  
         synthesis pathway.

- Ligands of the catalyst precursor may include one or  
         more functional groups selected from carboxylates, alkoxides,  
35        ketones, diketones, amines, amides, alkyls and aryls.  
         Suitable ligands include methyl, cyclohexyl, carbonyl,  
         cyclopentadienyl, cyclooctadiene, ethylene beta-diketones,  
         phosphines, organophosphorous ligands, polyethers,  
         dithiocarbamates, macrocyclic ligands (e.g., crown ethers) or

benzene ligands, or a mixture or two or more of thereof. In preferred embodiments, the catalyst precursor ligand and the carbon source are the same material, for example a metal carbonyl precursor with carbon monoxide feed source.

5 Ferrocene is a preferred catalyst precursor, since it is available at low cost and has relatively low toxicity.

Typically, organometallic species have better solubility in supercritical fluids than carbonyl species, and an organometallic species having optimum solubility may be  
10 selected, for example to ensure that the catalyst concentration in the furnace is not too high. Catalyst precursor concentration control can be effected by passing supercritical fluid through a vessel containing catalyst precursor.

15 Alternatively, the ligand may have a more complicated structure including multiple double bonds and linked aromatic rings, particularly five or six membered rings. Such structures may help to nucleate growing nanomaterials.

The catalyst precursor may be a multimetal atom cluster,  
20 such as triiron dodecylcarbonyl.

Suitably, the supercritical fluid is carbon dioxide or another fluid which does not act as a carbon source in the nanomaterial forming reaction. The supercritical fluid may alternatively be a hydrocarbon or other carbon-containing  
25 feedstock such as carbon monoxide, benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene, methane, ethane, propane, butane, pentane, hexane, cyclohexane, ethylene, propylene, acetylene, aldehydes such as formaldehyde or acetaldehyde, ketones such as acetone, or  
30 alcohols such as methanol or ethanol, or a mixture of two or more thereof.

The use of a carbon-containing feedstock as the supercritical fluid has two advantages. First, the yield-reducing reaction of carbon nanotube product with carbon  
35 dioxide supercritical fluid to form toxic carbon monoxide (which can take place within the furnace under certain temperature, pressure and concentration regimes) is avoided. Second, there is no need to introduce a separate carbon source, and the process is thereby simplified.

As a further alternative, a diluent gas such as argon, a dopant gas such as nitrogen, or an etchant gas for amorphous carbon such as ammonia may be used as the supercritical fluid.

Optionally, the solution may contain a suspended finely divided substrate material. The substrate material will help to nucleate and stabilise small metal clusters. In the most straightforward case, the substrate particles are simply finely ground powders, for example of silica or alumina. Finer materials may be generated by a range of methods known to those skilled in the art, such as fuming, colloidal processing, spray-drying, hydrothermal processing and so on. Particular benefit for the production of nanotubes may be derived by using structured substrate particles, particularly mesoporous silicas, anodised alumina membranes, or zeolites. These materials have channels of similar dimensions to nanotubes, and can further guide both the deposition of, catalyst and synthesis of nanotubes.

Alternatively, substrate particles may be introduced into the furnace separately, for example in their own carrier. A particularly preferred approach is to use so-called POSS (polyhedral oligomeric silsesquioxane) compounds as the catalyst-substrate particles. In this case the distinction between catalyst and substrate is rather blurred, as POSS compounds are themselves molecular silica-based materials. A POSS molecule can act as a site for catalyst formation in situ.

The advantages of using a POSS are numerous. They have a very high surface area. Their diameters are around 1 nm (the same size as single wall nanotubes) but are tuneable as different POSS molecules have different sizes. They can be monodisperse (have specific molecular weights) and hence have the potential to generate well-defined products. As they have molecular character, they may be liquid or may be dissolved in the supercritical fluid or a suitable liquid carrier (and may potentially even be evaporated directly) for injection into the furnace. They have excellent thermal stability in themselves. They have the potential to form well-defined derivatives that potentially add catalytic metallic particles



(for example iron). Generally a single POSS molecule will constitute a particle of substrate for nanotube growth.

The finely divided substrate particles preferably have a size not smaller than 1 nm, e.g. not less than 5 nm. They may contain not less than 10 atoms, e.g. not less than 15 to 20 atoms, perhaps not less than 50 atoms or 75 atoms. The substrate is fed to the zone in which the catalyst precursor is decomposed and preferably is essentially unchanged in the step of generating supported-catalyst particles, except for the deposition thereon of the catalyst material. However, some chemical modification of the substrate particles during the formation of the supported-catalyst particles is permissible, e.g. the removal of surface chemical groups or solvating chemical side chains. Preferably, the size of the substrate particles remains substantially unchanged.

The presence of the substrate particles during the decomposition of the catalyst precursor serves to lower the nucleation energy of the catalyst atoms and to control the size and shape of the catalyst cluster so formed.

Alternatively, a substrate precursor, for example a silicon-containing material such as tetramethyl orthosilicate or tetraethyl orthosilicate, may be contained in the solution. Such a precursor will decompose in the furnace to form a finely divided substrate material.

Suitably, formation of the carbon nanomaterials takes place at a temperature of from 650 °C to 1250 °C, e.g. 850 °C to 1100 °C.

To stimulate decomposition of the catalyst precursor material, an additional energy source (over and above the temperature of the furnace) may be locally applied. Such a source is preferably an intense light source, for example a laser or an intense non-coherent light source such as a flash discharge lamp. Preferably, the light source is an ultraviolet light source. Where the solution is expanded as it enters the furnace, the light source may be applied to the solution immediately before expansion. This will cause the catalyst precursor dissolved in the solution to undergo photolysis just before entering the hot zone of the furnace which may help to

release the metal atoms from the precursor compound. For example, UV photolysis of metal carbonyls can strip the CO units away from the metal. Bare metal atoms and clusters are more reactive to the hydrocarbon feedstock than coordinated  
5 atoms and clusters. Alternatively, the additional energy source may be a plasma discharge or an arc discharge formed in the presence of the catalyst precursor material.

Optionally, the catalyst precursor is introduced to the furnace at a lower temperature than that used for the majority  
10 of nanotube growth, in order, for example, to allow a period of time for catalyst particle ripening and hence to control whether single walled or multi walled carbon nanotubes are formed.

Preferred gas pressures for the feedstock are from 0.1  
15 to 50 bar A, preferably from 0.5 to 5 bar A, more preferably 1 to 2 bar A. The ratio of catalyst to carbon source fed to the furnace is preferably less than 1:100, e.g. 1:100 to 1:500.

In a second aspect, the present invention relates to the use of a supercritical fluid as a carrier for a catalyst or  
20 catalyst precursor for catalysing the formation of carbon nanomaterials.

In a third aspect, the present invention relates to a method of synthesis of carbon nanomaterials, comprising the steps of:  
25 preparing a solution of a catalyst or a catalyst precursor in a liquified gas, the catalyst or catalyst precursor being capable respectively of catalysing the formation of carbon nanomaterials from a carbon source or of reacting to form a catalyst having such a capability;  
30 expanding the solution to produce particles of catalyst or catalyst precursor; and  
heating the catalyst or catalyst precursor particles with a carbon source in a furnace to produce carbon nanomaterials.

The wording "liquified gas" is used to indicate a  
35 pressurised liquid which would be gaseous at room temperature and pressure. The use of a liquified gas solvent extends the range of possible solvents which may be used. For example, methane, ethane, propane, butane, pentane, ethylene or acetylene below their respective critical temperatures might

be used as the solvent. These molecules have cleaner decomposition pathways than typical hydrocarbon solvents. The liquified gas is under pressure and this provides a useful means of providing rapid expansion or atomisation of the precursor solution, compared to conventional solvent systems. The liquified gas solvent may form a supercritical fluid before expansion if it is heated, this being one way of preparing the solution in a supercritical fluid according to the first aspect of the invention. Alternatively, the liquefied gas may be expanded by pressure drop without significant heating.

In a fourth aspect, the present invention relates to a method of synthesis of carbon nanomaterials, comprising the steps of:

preparing a solution of a catalyst or a catalyst precursor in a pressurised RTP liquid, the catalyst or catalyst precursor being capable respectively of catalysing the formation of carbon nanomaterials from a carbon source or of reacting to form a catalyst having such a capability;

expanding the solution to produce particles of catalyst or catalyst precursor; and

heating the catalyst or catalyst precursor particles with a carbon source in a furnace to produce carbon nanomaterials.

The wording "pressurised RTP liquid" is used to indicate a material which would be liquid at room temperature and pressure, but which is heated to a temperature where it would be gaseous at atmospheric pressure and liquified under pressure. Examples of pressurised RTP liquids are hexane and ethanol. Pressurised RTP liquids may be expanded by pressure drop without significant heating in a similar manner to liquified gases.

The invention will be further illustrated by the following examples, with reference to the Figures, in which:

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Figure 1 shows the apparatus used in Example 2.

Figure 2 shows the apparatus used in Example 3.

Example 1

Iron pentacarbonyl beads are placed within a long tubular pressure vessel. Using a high pressure pump with a chilled pump head, the tube is then filled with carbon dioxide and maintained at 1000 psi at 40 °C during operation, thus forming the supercritical carbon dioxide phase. Additional carbon dioxide is pumped along the tube and becomes saturated with the iron catalyst precursor. In order to ensure continuous operation, two pressure vessels are arrayed in parallel; when the precursor is exhausted from one tube, flow is switched to the other whilst the first tube is recharged. The solution is passed from the active pressure reservoir into a CVD furnace held at 1000 °C and 1.5 atm, by means of an expansion nozzle where it mixes turbulently with methane separately introduced into the furnace and pre-heated to near furnace temperature. As the temperature of the iron pentacarbonyl rises it decomposes and reacts with the hydrocarbon to nucleate the growth of small diameter nanotubes. The nanotubes continue to grow as they pass along the CVD furnace and are collected by cyclonic separation and filtration after leaving the furnace.

Example 2

Example 2 is carried out using the apparatus shown in Figure 1. This apparatus comprises a CO<sub>2</sub> cylinder 10 with dip stick (not shown), a chiller 12 and a compressor 14. The chiller 12 and compressor 14 can be combined by using a chilled HPLC pump.

The compressor 14 is linked to a heat pipe 16, used until the entry into the furnace, flow valves 18 and a container 20 holding ferrocene and provided with a fine filter at each end to prevent undissolved ferrocene from being swept into the system.

A spiral pipe 22, used to give suitable time for the catalyst and supercritical fluid to become well mixed, leads from a flow valve 18 to a safety pressure valve 24, a back pressure regulator or needle valve 26 and a furnace 28

containing a reaction vessel 36 made from silica with metal end plates and with a diameter of about 70 mm which is orientated vertically so that the gas flows downwards.

5 The reaction vessel 36 contains a deflector 30 to prevent the super-critically expanded gas passing straight through the furnace. The outlet of the reaction vessel 36 is connected to a filter bag 32 to collect the nanomaterial produced.

10 The supercritical fluid stream is split just before container 20, such that some passes through the catalyst precursor while the rest goes through a separate bypass pipe 34. These streams rejoin after the container 20 and therefore by varying the flow valves 18 the concentration of the catalyst precursor in the supercritical fluid can be controlled. As an alternative to the use of the container 20  
15 and the catalyst bypass pipe 34, an HPLC pump (not shown) may be used to inject catalyst directly into the supercritical fluid.

The apparatus of Figure 1 is used with carbon dioxide as the supercritical fluid, methane as the carbon source and  
20 ferrocene as the catalyst precursor. The methane and hydrogen enter the furnace 28 from the cold end, while the supercritical gas is expanded through a suitable expansion nozzle directly in the hot zone. The catalyst bypass pipe 34 is closed such that the supercritical fluid is saturated with  
25 ferrocene. The carbon dioxide is used at a flow rate of 1 ml/min at supercritical conditions. The methane and hydrogen both enter the furnace 28 at a flow rate of 4l/min at room temperature and atmospheric pressure. The supercritical fluid containing the catalyst precursor expands into the furnace 28,  
30 where the deflector 30 is used to prevent the faster particles from passing straight through the furnace 28. Nanotubes are found to be produced in the hot zone.

### Example 3

35

Example 3 is carried out using the apparatus shown in Figure 2, which is similar to that of Figure 1 except that a chilled HPLC pump 38 is used instead of the chiller 10 and compressor

12 and the catalyst precursor is injected into the  
supercritical fluid using an HPLC pump 40 instead of passing  
the supercritical fluid through the container 20. The  
catalyst precursor which is injected consists of tris(2,4-  
5 pentanedionato)iron(III) dissolved in methanol.

The apparatus of Figure 2 is used with methanol as the  
supercritical fluid and as the carbon source and with tris  
[2,4-pentanedionato] iron (III) as the catalyst precursor.  
The nanotubes are found to be formed in the hot zone.

10

#### Example 4

Ferrocene beads are placed within a long tubular  
pressure vessel. Using a high pressure pump with a chilled  
15 pump head, the tube is filled with propane (which acts as  
liquefied gas and as carbon source) and maintained at 200 psi  
at 25 °C during operation, forming a liquified propane gas  
phase saturated with ferrocene catalyst precursor. Additional  
propane is pumped along the tube and, in turn, becomes  
20 saturated with the ferrocene catalyst precursor. In order to  
ensure continuous operation, two pressure vessels are arrayed  
in parallel; when the precursor is exhausted from one tube,  
flow is switched to the other whilst the first tube is  
recharged. The solution is passed from the active pressure  
25 reservoir into a CVD furnace held at 800 °C and 1.5 atm by  
means of an expansion nozzle where it mixes turbulently with  
argon gas separately introduced into the furnace and pre-  
heated to near furnace temperature which is used as a diluent  
and thermal reservoir. As the temperature of the ferrocene  
30 rises it decomposes and reacts with the propane to nucleate  
the growth of small diameter nanotubes. The nanotubes  
continue to grow as they pass along the CVD furnace and are  
collected by cyclonic separation and filtration after leaving  
the furnace.

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These embodiments of the invention have several advantages over the prior art.

Since supercritical fluids expand to fill space, a large expansion will be experienced as the supercritical solution of precursor enters the furnace. The precursor thus enters the furnace with excellent dilution and separation, meaning that premature cluster formation is prevented, without contaminating the furnace with unwanted hydrocarbons. The expansion will also cool the precursor as it enters the furnace, helping to prevent premature decomposition and cluster formation before the precursor is mixed with the hot hydrocarbon feedstock. The expansion also generates a region of high turbulence in the furnace which enhances mixing of the precursor and hydrocarbon. Expansion is typically supersonic (which helps achieve a truly molecular dispersion).

The solubility of the precursor is a function of the pressure of the supercritical fluid. Control of the pressure of the supercritical fluid may thus be used to control the concentration of precursor in a saturated system.

The use of a supercritical fluid minimises the opportunities for liquid droplet formation and subsequent surface evaporation that could otherwise concentrate the precursor and form an undesirably large catalyst cluster. It is preferred that the expansion is rapid to avoid any liquid to gas transition.

Carbon dioxide is essentially inert under the conditions experienced in the furnace, and supercritical carbon dioxide is a relatively safe, non-flammable material that is formed at modest temperatures and pressures. Furthermore, carbon dioxide is a well-explored and understood supercritical system and has reasonable solubilities for metallocene and carbonyl precursors that are most commonly used. Use of supercritical carbon dioxide as an inert carrier allows the active hydrocarbon to be injected elsewhere.

Whilst the invention has been described with reference to a particular preferred embodiment, it will be appreciated that many variations and modifications of the embodiment described will be possible within the scope of the invention.

Claims

- 5 1. A method of synthesis of carbon nanomaterials,  
comprising the steps of:  
preparing a solution of a catalyst or a catalyst  
precursor in a supercritical fluid, or of a  
10 supercritical fluid in a catalyst or a catalyst  
precursor, the catalyst or catalyst precursor being  
capable respectively of catalysing the formation of  
carbon nanomaterials from a carbon source or of reacting  
to form a catalyst having such a capability;  
15 expanding the solution to produce particles of catalyst  
or catalyst precursor; and  
heating the catalyst or catalyst precursor particles  
with a carbon source to produce carbon nanomaterials.
2. A method as claimed in Claim 1, wherein the heating is  
20 carried out in a furnace.
3. A method as claimed in Claim 2, wherein the solution is  
expanded as it enters the furnace.
- 25 4. A method as claimed in Claim 1 or Claim 2, wherein the  
carbon source is carbon monoxide, benzene, toluene,  
xylene, cumene, ethylbenzene, naphthalene, phenanthrene,  
anthracene, methane, ethane, propane, butane, pentane,  
hexane, cyclohexane, ethylene, propylene, acetylene,  
30 formaldehyde, acetaldehyde, acetone, methanol, or  
ethanol or a mixture of two or more thereof.
5. A method as claimed in any one of the preceding claims,  
wherein a transition metal catalyst precursor is used.
- 35 6. A method as claimed in Claim 4, wherein the transition  
metal catalyst precursor comprises copper (Cu), chromium  
(Cr), molybdenum (Mo), tungsten (W), iron (Fe), cobalt  
(Co), nickel (Ni), ruthenium (Ru), rhodium (Rh),



palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt), a metal from the lanthanide or actinide series, or a mixture of two or more thereof.

- 5    7.    A method as claimed in Claim 5, wherein the transition metal catalyst precursor comprises a 50/50 mixture by weight of Ni and Co, Fe and Ni, or Fe and Mo.
- 10    8.    A method as claimed in Claim 5 or Claim 6, wherein the transition metal catalyst precursor comprises methyl, cyclohexyl, carbonyl, cyclopentadienyl, cyclooctadiene, ethylene or benzene ligands, or a mixture of two or more thereof.
- 15    9.    A method as claimed in any one of the preceding claims, wherein the supercritical fluid is carbon monoxide, benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene, anthracene, methane, ethane, propane, butane, pentane, hexane, cyclohexane, ethylene, propylene, acetylene, formaldehyde, acetaldehyde, acetone, methanol, or ethanol or a mixture of two or more thereof.
- 20    10.   A method as claimed in any one of Claims 1 to 8, wherein the supercritical fluid is carbon dioxide.
- 25    11.   A method as claimed in any one of the preceding claims, wherein an intense light source is applied to the solution immediately before expansion.

12. A method as claimed in Claim 9, wherein the light source is an ultraviolet light source.
- 5 13. A method as claimed in any one of the preceding claims, wherein the solution contains a finely divided substrate material.
- 10 14. A method as claimed in any one of the preceding claims, wherein the solution contains fumed silica or polyhedral oligomeric silsesquioxanes (POSS).
- 15 15. A method as claimed in any one of the preceding claims, wherein the solution contains a substrate precursor material capable of reaction to produce a finely divided substrate material.
- 20 16. The use of a supercritical fluid as a carrier for a catalyst or catalyst precursor for catalysing the formation of carbon nanomaterials.
- 25 17. A method of synthesis of carbon nanomaterials, comprising the steps of:  
preparing a solution of a catalyst or a catalyst precursor in a liquified gas, or of a liquified gas in a catalyst or a catalyst precursor, the catalyst or catalyst precursor being capable respectively of catalysing the formation of carbon nanomaterials from a carbon source or of reacting to form a catalyst having such a capability;  
30 expanding the solution to produce particles of catalyst or catalyst precursor; and  
heating the catalyst or catalyst precursor particles with a carbon source to produce carbon nanomaterials.

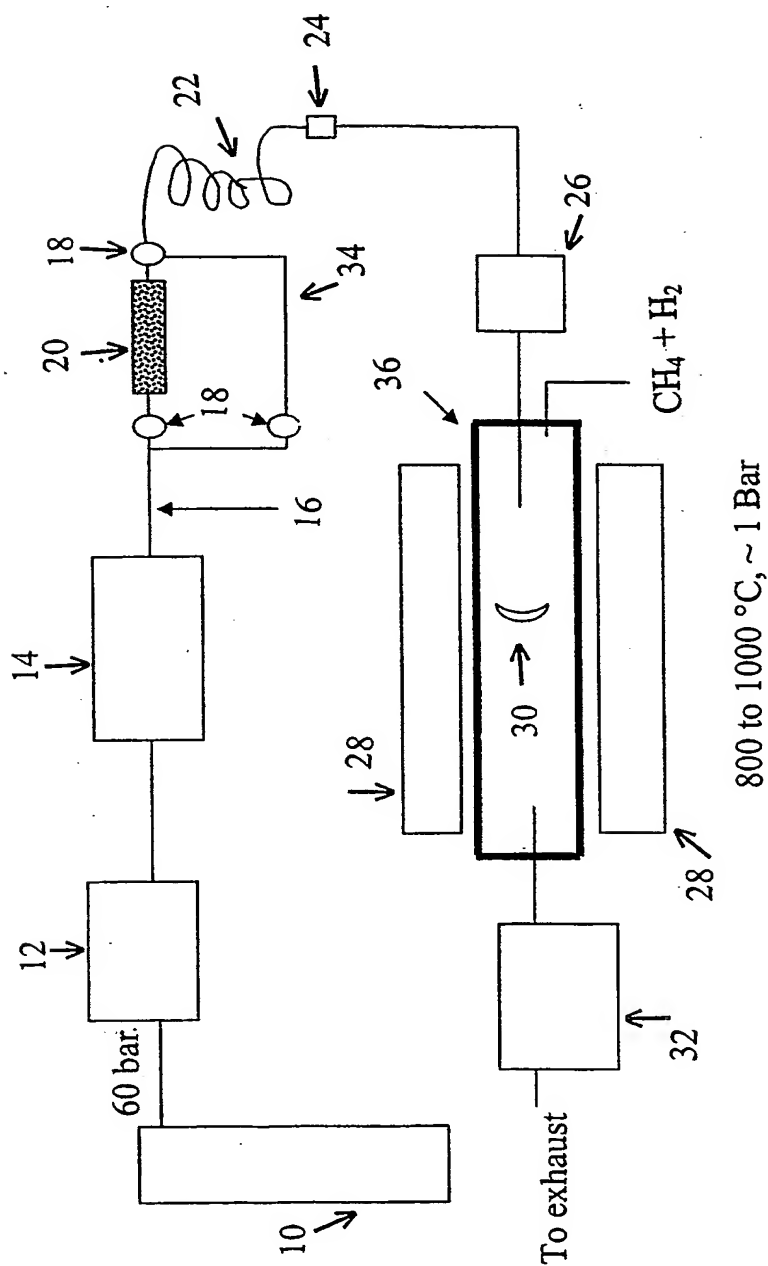
$\frac{1}{2}$ 

FIG. 1

2/2

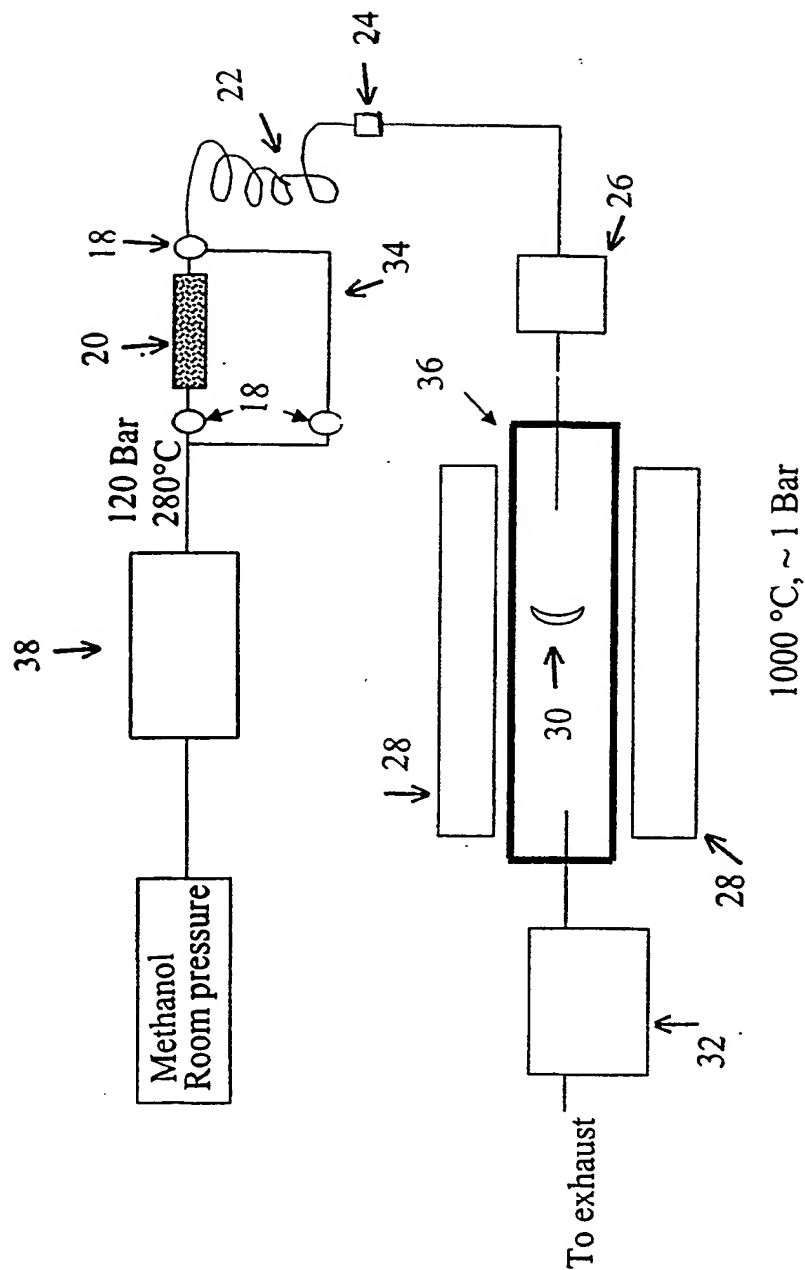


FIG. 2.

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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1 April 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF SYNTHESIS OF CARBON NANOMATERIALS

(57) Abstract: A method of synthesis of carbon nanomaterial comprises the steps of: preparing a solution of a catalyst or a catalyst precursor in a supercritical fluid, or of a supercritical fluid in a catalyst or a catalyst precursor, the catalyst or catalyst precursor being capable respectively of catalysing the formation of carbon nanomaterials from a carbon source or of reacting to form a catalyst having such a capability; expanding the solution to produce particles of catalyst or catalyst precursor; and heating the catalyst or catalyst precursor particles with a carbon source to produce carbon nanomaterials.

WO 2004/007361 A3

# INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/GB 03/03115

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 02 079082 A (UNIV RICE WILLIAM M) 10 October 2002 (2002-10-10) claims 1,2,3,4,5,6,18,19,,24,6 page 11, line 27 -page 12, line 38 figures 1-6	1-6, 8-11,16
A	----- DATABASE WPI Section Ch, Week 200273 Derwent Publications Ltd., London, GB; Class E36, AN 2002-679265 XP002268038 & KR 2002 025 101 A (NANOTECH CO LTD), 3 April 2002 (2002-04-03) abstract ----- -/-	17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

26 January 2004

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/GB 03/03115

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PROKUDINA N A ET AL: "CARBON NANOTUBE RLC CIRCUITS" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 12, no. 19, 2 October 2000 (2000-10-02), pages 1444-1447, XP000966760 ISSN: 0935-9648 the whole document ---	17
A	WO 00 26138 A (BRONIKOWSKI MICHAEL J ;SMALLEY RICHARD E (US); UNIV RICE WILLIAM M) 11 May 2000 (2000-05-11) claims 1,11,13 ---	17
A	SONGSASEN, APISIT ET AL: "Preparation of carbon nanotubes by nickel catalyzed decomposition of liquefied petroleum gas (LPG)" KASETSART JOURNAL: NATURAL SCIENCES (2001), 35(3), 354-359 , 2001, XP008026718 the whole document ---	17
A	CAO A ET AL: "An effective way to lower catalyst content in well-aligned carbon nanotube films" CARBON, XX, XX, vol. 39, no. 1, January 2001 (2001-01), pages 152-155, XP004319836 ISSN: 0008-6223 page 153 ---	1
A	CHATTOPADHYAY P GUPTA R B: "Supercritical CO2-based production of fullerene nanoparticles" INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, AMERICAN CHEMICAL SOCIETY. WASHINGTON, US, vol. 39, no. 7, 5 May 2000 (2000-05-05), pages 2281-2289, XP002960657 ISSN: 0888-5885 the whole document -----	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Int. application No.  
PCT/GB 03/03115

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.



## INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 03 03115

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

### 1. Claims: 1-16

Claims 1 to 15 are directed to a method for preparing carbon nanomaterials. This method comprises the use of a solution of the catalyst source in a supercritical fluid or of a supercritical fluid in the catalyst source.

The claim 16 refers to the use of a supercritical fluid as a carrier for a catalyst source.

### 2. Claim : 17

The claim 17 refers to a method of synthesis of carbon nanomaterials. This method comprises the use of a solution of the catalyst source in a liquefied gas or of a liquefied gas in a catalyst source.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No  
PCT/JP 03/03115

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 02079082	A	10-10-2002	US 2002102203 A1	01-08-2002
			US 2002102194 A1	01-08-2002
			WO 02079082 A2	10-10-2002
			WO 02060813 A2	08-08-2002
			US 2002102193 A1	01-08-2002
KR 2002025101	A	03-04-2002	NONE	
WO 0026138	A	11-05-2000	AU 1603300 A	22-05-2000
			CA 2350099 A1	11-05-2000
			CN 1373736 T	09-10-2002
			EP 1137593 A1	04-10-2001
			WO 0026138 A1	11-05-2000
			US 2003190277 A1	09-10-2003